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(54) CERAMIC DECALCOMANIA AND METHOD OF MAKING

(71) We, THE MEYERCORD CO., a Corporation organized and existing under the Laws of the State of Delaware, United States of America, of 365 East North Avenue, Carol Stream, City of Wheaton, Illinois 60187, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates generally to improvements in decalcomania for decorating a ceramic article, such as glassware, chinaware, porcelain ware, pottery, and the like and to a method of making decalcomania.

Heretofore, decalcomania have been devised, for use on ceramic articles, which after application to ceramic articles and subsequent firing, provide a clear protective layer of low melting point glass over a pigmented ceramic design, so that the design is protected against chemical detergents and abrasion encountered during washing (see U.S. Patent No. 2,734,840). Decalcomania adapted to provide such a clear protective layer over the design are herein referred to as being "of the type specified". Decalcomania of the type specified, however, have been limited to water release decalcomania in which the ceramic portions of the decalcomania are applied face-up on a thin layer of water-soluble gum supported on a paper carrier or backing sheet. Water release type decalcomania have serious disadvantages which make their commercial use relatively difficult and expensive.

It is therefore an object of the present invention to provide an improved decalcomania of the type specified which can be applied more readily and at a lower unit cost than the prior art decalcomania.

According to one aspect of the invention there is provided a decalcomania for application to a ceramic article comprising: a flexible base sheet substantially impervious to wax, a wax coating on said sheet, a layer of unpigmented finely divided low melting point glass supported by said wax coating, a pigmented design layer, comprising inorganic colouring material, supported by said layer of low melting point glass, said layer of unpigmented glass being adapted, on heating at a temperature above the fusion point of said glass to form an impervious clear protective glass film over said pigmented design, and said pigmented design layer incorporating, or having on the surface thereof remote from said layer of unpigmented glass, thermoplastic organic adhesive material which is adapted to adhere to a ceramic article placed in contact therewith when said ceramic article is at a temperature at which the flexible base sheet is released from the layer of unpigmented finely divided low melting point glass.

Another object of the present invention is to provide an improved method of making a decalcomania for application to an article.

According to another aspect of the invention there is provided a method of making a decalcomania for application to a ceramic article comprising, forming a coating of wax on a flexible base sheet which is substantially impervious to the said wax, applying to said coating of wax a layer of unpigmented finely divided low melting point glass, forming a pigmented design layer on the surface of said unpigmented layer of glass, said layer of inpigmented glass being adapted, on heating to a temperature above the fusion point of said glass to form an impervious clear protective glass film over said pigmented design, and providing incorporated in said design layer, on the exposed surface of said design layer, thermoplastic organic adhesive material which is adapted to adhere to a ceramic article placed in contact therewith when said ceramic article is at a temperature at which the flexible base sheet is released from the layer of unpigmented finely divided low melting point glass.

A still further object of the present invention is to provide an improved method of applying a ceramic decalcomania to an article.

According to a yet further aspect of the invention there is provided a method of providing a design on a ceramic article

which comprises applying a decalcomania according to the first mentioned aspect of the invention, or made by the method according to the invention, to said ceramic article after heating the latter to a temperature at which the base sheet is released from the layer of unpigmented finely divided low melting point glass, the decalcomania being applied to the ceramic article with said thermoplastic material, or the design layer incorporating such material, in contact with the ceramic article, removing said base sheet and thereafter heating said ceramic article to a temperature above the temperature at which said low melting point glass fuses and below the softening point of said ceramic article, whereby said unpigmented glass forms an impervious clear protective glass film over said pigmented design and is fusibly jointed to the ceramic article.

Embodiments of the invention are described below with reference to the accompanying drawings wherein:

Figure 1 is a diagrammatic cross-sectional representation of a decalcomania embodying the present invention; and

Figure 2 is a diagrammatic cross-sectional representation of a modified form of decalcomania embodying the present invention.

In general terms, in the preferred embodiments of the invention a decalcomania for application to a ceramic article is formed by forming a coating of wax on a flexible base sheet which is substantially impervious to the wax, applying to said coating of wax a coating of a low melting point glass having the composition thereof adjusted so that the physical properties thereof, and particularly the coefficient of thermal expansion, match as closely as possible the physical characteristics of the ceramic article to which the decalcomania is to be applied, and applying over the coating of low melting point glass a face-down pigmented design with an adhesive layer applied to the outer surface of the design or admixed therewith.

Thus, with reference to Figures 1 and 2, there is described below an improved vitreous decalcomania or transfer which is adapted for manufacture by any suitable method, e.g. silk screen printing, lithography, rotogravure or letter press printing. The decalcomania has a releasable backing comprising, in the preferred embodiments, a paper sheet 1 with a barrier layer or coating 2 which renders one side of the paper less porous and substantially impervious to wax. The barrier coated paper is also provided with a superimposed heat-release coating 3 of wax or wax-like material. A powdered layer 4 of components which form on fusion a clear protective glass layer having a composition and properties as hereinafter described is applied directly over the wax coating 3. In the embodiment of Figure 1, a pigmented design layer 5, is disposed directly against the layer 4, with the design layer 5 including powdered vitreous material and incorporating inorganic colouring material, and being arranged to provide the desired ornamentation or text matter. Over the outermost side of the pigmented design 5 is provided a layer 6 of a suitable thermoplastic or heat activatable adhesive material which serves as a temporary binder for securing the design layer 5 and layer 4 to the ceramic article being decorated until heating to effect fusibly joining the design 5 with the protective layer 4 to the ceramic article.

In the embodiment illustrated in Figure 2 of the drawings, the pigmented design layer 7 is formed of inorganic colouring material without powdered vitreous material and has a thermoplastic organic adhesive material admixed therewith so that there will be a tacky film of adhesive formed in situ at the surface of the design layer when the decalcomania is heated during application thereof. Although not shown in the drawings, the bottom or opposite side of the paper sheet in the embodiments of Figs. 1 and 2 may also have a wax coating or the like in order to facilitate stacking of individual transfers one against the other without sticking or blocking and thereby avoiding the use of separate slip sheets when it is desired to stack a group of transfers.

U.S. Patents No. 2,970,076 and No. 3,007,829 show several ways of preparing a suitable flexible base sheet with a wax coating and pigmented ceramic design layer with associated adhesive film for use in the present invention.

It has been found that the layer 4 can be applied directly on the wax or equivalent heat-release coating 3 without using a clear resinous film usually applied over the heat-release coating, although a clear resinous film can be used without departing from the scope of the present invention. It has also been found that the pigmented design layer 5 can be formed directly on the layer 4 without first applying a resinous film over the layer 4.

In preparing the layer 4 on which the pigmented design layer 5 is directly formed it is important that the layer 4 which is normally applied as a powdered prefused glass or flux is compounded so that the physical properties thereof, and particularly the coefficient of thermal expansion, match as closely as possible the physical properties, and particularly the coefficient of thermal expansion, of the ceramic article to which the decalcomania is applied. Since the layer 4 should have a relatively low melting point to permit fusion thereof below a temperature

which will cause discolouration of the pigmented design layer 5, the ingredients of the glass should be prefused to provide a uniform melt after which the fused frit is finally divided to permit application of a uniform layer either in powdered form or in a suitable liquid carrier of the type described in U.S. Patent No. 2,970,076. A suitable low melting point glass which comprises the basic ingredient of the layer is unpigmented lead borosilicate glass which has incorporated therewith one or more metal oxides in an amount sufficient to adjust the coefficient of thermal expansion to match as closely as possible that of the particular ceramic article to which the decalcomania is to be applied. Among the metal oxides which can be added to a lead borosilicate glass to adjust the phsyical properties and particularly the coefficient of thermal expansion thereof are cadmium oxide, lithium oxide, calcium oxide, magnesium oxide, titanium oxide, aluminum oxide, sodium oxide, potassium oxide and zirconium oxide. The precise manner in which the coefficient of thermal expansion of the clear protective glass film is adjusted will depend on the composition of the glass flux and the ceramic article being decorated, and any of the various means known to those skilled in the art can be used.

The following specific example is given in order to further illustrate the present invention without, however, limiting the invention to the particular material or procedure used.

EXAMPLE I

A ceramic decalcomania for use on opalified glass having a coefficient of thermal expansion of about 10.7×10—6°C was prepared by the silk screen process on wax coated paper having as the barrier coating a layer of polyvinyl acetate manufactured substantially as shown in the U.S. Porth Patent No. 2,970,076. This paper consists of a 70—80 pound fully bleached Kraft stock treated with a barrier coat to prevent wax penetration and a wax coating consisting of approximately 4.5 pounds per ream of Carbowax 4000. On this wax-coated paper, in "face down" rotation was first deposited a very thin layer of clear glass flux through a 390 mesh polyester screen. The flux consisted basically of powdered unpigmented lead borosilicate with 1.0% by wt. cadmium oxide (CdO), 3.0% by wt. zirconium oxide (ZrO_2) and 3.0% by wt. aluminum oxide (Al_2O_3), and provided a coefficient of thermal expansion substantially that of the opalified glass base to be decorated. For screening purposes the flux was dispersed in 3-part organic resin vehicle at a ratio of $2\frac{1}{4}$ parts flux to 1 part vehicle. This 3-part organic vehicle was prepared from the materials sold under the Registered Trade Marks Elvacite 2044 and Elvacite 2045 (DuPont acrylic resins) and the material sold under the Registered Trade Mark Piccolastic A-5 (Pennsylvania Industrial Chemical polystyrene) in the approximate ratios of 2:2:0.6. These 3 resins were dissolved in an aromatic hydrocarbon solvent, such as, Solvesso 150.

Over the flux then were screened vitreous colours, also dispersed in the same vehicle as the flux, which formed the pigmented design. A 350 mesh polyester screen was used for each colour.

Finally, a heat activatable adhesive was screened over the entire design. This adhesive consisted of approximately equal parts of N-100 ethylcellulose (Hercules Chemical Co.) and the material sold under the Registered Trade Mark Piccolastic A-5. These resins were dissolved in a n-amyl alcohol and Solvesso 100. A 200 mesh polyester screen was used.

When applying the foregoing decalcomania to the surface of the opalified glassware base, the base was preheated to about 300°F (i.e. between 250°—325°F), the decalcomania placed with the thermoplastic adhesive-containing surface in contact with the base, rolled firmly into place, and the backing paper stripped away. On firing at a temperature sufficiently high to form a clear melt of the unpigmented flux layer but below the softening point of the opalified glass base being decorated, and preferably at a temperature of about 1300°F, a decorative design was formed on the glass base which had a top or outer impervious film of clear protective glass which gave added protection and gloss to the decorative design.

It should be understood that instead of the prefused lead borosilicate glass the low melting point unpigmented glass flux employed as the basic ingredient for the protective layer 4 can be one of the other low melting point glass fluxes, such as the potash-lead glasses; lead glass, flint glass, and crown glass, depending on the intended use of the ceramic article being decorated.

It will also be understood that by selecting as the heat release layer or the thermoplastic adhesive layer other compositions which are thermally activated at a temperature higher or lower than those used in the foregoing example, it is possible to have the ceramic article to be decorated at a temperature other than the 300°F temperature used therein when the ceramic decalcomania is applied. For example, when polyethylene glycol polymers are used as the heat release layer, a normally solid polyethylene glycol is used which softens sufficiently to release the design when the decalcomania is applied to an article heated to a temperature between about 100°F and 350°F (see Akkeron U.S.

Patent No. 3,007,829). Thus, the term "wax" as used in the foregoing description and in the claims which follow refers not only to hydrocarbon type waxes but also to the synthetic wax-like products, such as that sold under the Registered Trade Mark "Carbowax" (Union Carbide Corporation) which is comprised of polyethylene glycols.

The term "pigmented design" as used in the description and claims refers to a design comprising one or more inorganic colours stable at the temperature to which the ceramic article is heated to effect fusion of the protective layer of low melting point glass of the decalcomania, with or with vitrifiable ingredients mixed therewith, in an organic resinous medium.

WHAT WE CLAIM IS:—

1. A decalcomania for application to a ceramic article comprising: a flexible base sheet substantially impervious to wax, a wax coating on said sheet, a layer of unpigmented finely divided low melting point glass supported by said wax coating, a pigmented design layer, comprising inorganic colouring material, supported by said layer of low melting point glass, said layer of unpigmented glass being adapted, on heating at a temperature above the fusion point of said glass to form an impervious clear protective glass film over said pigmented design, and said pigmented design layer incorporating, or having on the surface thereof remote from said layer of unpigmented glass, thermoplastic organic adhesive material which is adapted to adhere to a ceramic article placed in contact therewith when said ceramic article is at a temperature at which the flexible base sheet is released from the layer of unpigmented finely divided low melting point glass.

2. A decalcomania as claimed in claim 1, wherein said layer of unpigmented finely diivded low melting point glass has a coefficient of thermal expansion substantially matching that of said ceramic article.

3. A decalcomania as claimed in claim 2, which is adapted to be applied to a ceramic article of opalified glass and wherein said layer of unpigmented finely divided low melting point glass is lead borosilicate glass containing on a wt. basis 1% cadmium oxide (CdO), 3% zirconium oxide (ZrO_2) and 3% aluminum oxide (Al_2O_3).

4. A method of making a decalcomania for application to a ceramic article comprising, forming a coating of wax on a flexible base sheet which is substantially impervious to the said wax, applying to said coating of wax a layer of unpigmented finely divided low melting point glass, forming a pigmented design layer on the surface of said unpigmented layer of glass, said layer of unpigmented glass being adapted on heating to a temperature above the fusion point of said glass to form an impervious clear protective glass film over said pigmented design and providing incorporated in said design layer, on the exposed surface of said design layer, thermoplastic organic adhesive material which is adapted to adhere to a ceramic article placed in content therewith when said ceramic article is at a temperature at which the flexible base sheet is released from the layer of unpigmented finely divided low melting point glass.

5. A method as claimed in claim 4, wherein said layer of unpigmented low melting point glass has a coefficient of thermal expansion substantially matching that of said ceramic article.

6. A method as claimed in claim 4, wherein said layer of unpigmented low melting point glass is lead borosilicate glass containing on a weight basis 1% cadmium oxide (CdO), 3% zirconium oxide (ZrO_2) and 3% aluminum oxide (Al_2O_3).

7. A method of providing a design on a ceramic article which comprises the steps of applying a decalcomania as claimed in claim 1 or a decalcomania made by the method of claim 4, to said ceramic article after heating the latter to a temperature at which the base sheet is released from the layer of unpigmented finely divided low melting point glass, the decalcomania being applied to the ceramic article with said thermoplastic material, or the design layer incorporating such material, in contact with the ceramic article, removing said base sheet and thereafter heating said ceramic article to a temperature above the temperature at which said low melting point glass fuses and below the softening point of said ceramic article, whereby said unpigmented glass forms an impervious clear protective glass film over said pigmented design and is firstly joined to the ceramic article.

8. A method as claimed in claim 7 wherein said unpigmented low melting point glass has a coefficient of thermal expansion substantially matching that of said ceramic article.

9. A method as claimed in claim 7 or 8, at which the temperature of the ceramic article when the decalcomania is applied thereto is between 100°F and 350°F.

10. A method as claimed in claim 7, 8 or 9, wherein said ceramic article is of opalified glass and wherein said layer of unpigmented finely divided low melting point glass is borosilicate glass containing on a wt. basis 1% cadmium oxide (CdO), 3% zirconium oxide (ZrO_2) and 3% aluminum oxide (Al_2O_3).

11. A method as claimed in claim 10, wherein said opalified glass article with said layer of unpigmented finely divided low melting point glass and the pigmented de-

sign adhesively held on the surface thereof is heated to a temperature of about 1300°F; whereby said impervious clear protective glass film is formed over the pigmented design on said opalified glass.

12. A decalcomania for application to a ceramic article substantially as hereinbefore described with reference to and as shown in Figure 1 of the accompanying drawings.

13. A decalcomania for application to a ceramic article substantially as hereinbefore described with reference to and as shown in Figure 2 of the accompanying drawings.

14. A method of making a decalcomania for application to a ceramic article, substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

15. A method of making a decalcomania for application to a ceramic article, substantially as hereinbefore described with reference to Figure 2 of the accompanying drawings.

16. A method of providing a design on a ceramic article, substantially as hereinbefore described with reference to the accompanying drawings.

17. A ceramic article having a design thereon, formed by the method of any of claims 7 to 11 or 16.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

FIG. 1

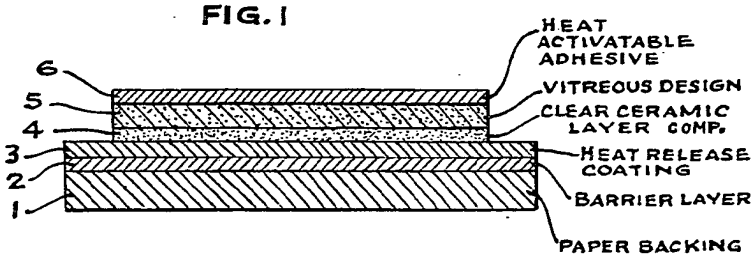

FIG. 2